Issues Impacting Refractory Service Life in Biomass/Waste Gasification

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ABSTRACT

Different carbon sources are used, or are being considered, as feedstock for gasifiers; including natural gas, coal, petroleum coke, and biomass. Biomass has been used with limited success because of issues such as ash impurity interactions with the refractory liner, which will be discussed in this paper.

Key words: Gasification, gasifier, refractory, biomass, waste, alkali

INTRODUCTION

Gasifiers were first used in industry around 1800; but the modern high temperature, high pressure units currently used by the chemical, petrochemical, and power industries were first developed and put into commercial service in the 1950's and 1960's; and are greatly improved technologically over those of the past [1]. An example of an air cooled slagging gasification system, with the ability to produce a variety of products, from electricity to chemicals, is shown in figure 1. Complex issues determine the type of gasification process selected for a given carbon feedstock, and a number of technical issues remain to be resolved before this technology will be widely adopted for carbon feedstock such as biomass or waste materials. Among these issues are improved lining materials with adequate service life for the gasification chamber.

In its simplest form, a gasifier is nothing more than a containment vessel used to react a carbon-containing material with oxygen and water (steam) under reducing conditions (shortage of oxygen) using fluidized-bed, moving-bed, or entrained-flow technology. The gasification process produces CO and H_2 as the primary products (also called synthesis gas or syngas), along with by-products of CO_2 and minority gases according to the following simplified equation:

$$C + H_2O\ (gas) + O_2 \rightarrow CO + H_2 + CO_2 + \text{minority gases} + \text{by-products} \quad \text{[equation 1]}$$

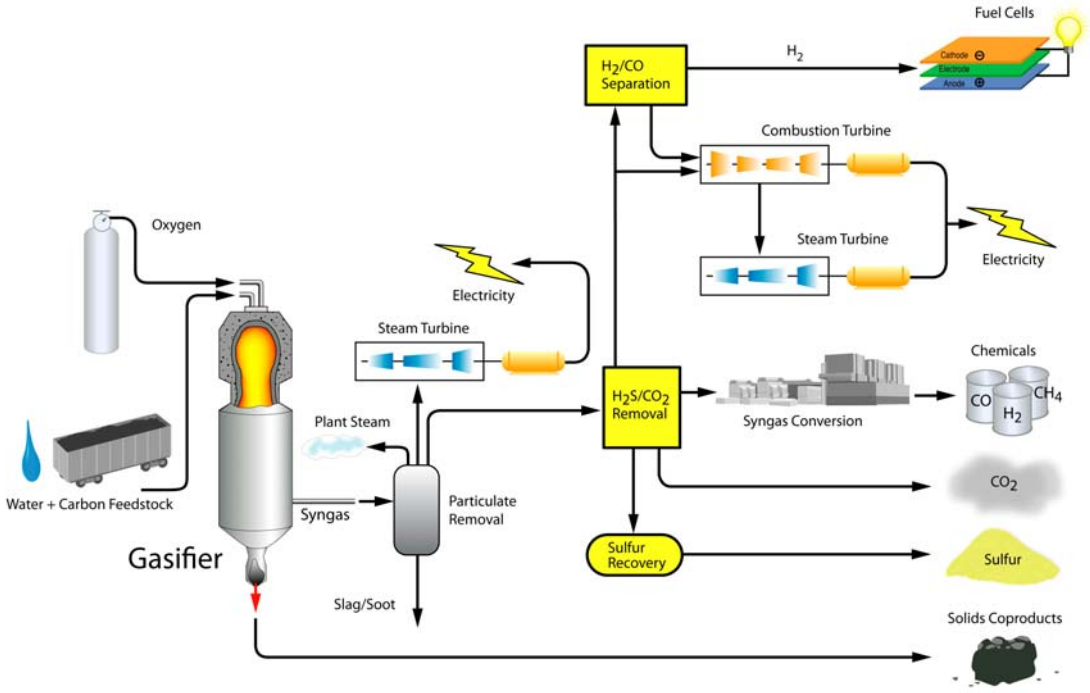

Figure 1: An air cooled slagging gasification plant.

Gasification is considered a non-catalytic process that involves a number of endothermic and exothermic reactions, with the overall process being exothermic [1]. In the reducing environment of gasification (oxygen partial pressure can be as low as 10^{-10} atm.); excess carbon from the feedstock becomes a by-product of the process. Ideally, the amount of excess carbon should be small, about 1.0 wt pct; but is dependent upon variables such as the gasifier type, carbon feedstock, O_2/C ratios, and the level of carbon beneficiation [2, 3]. By-products of gasification depend on process variables and impurities in the carbon feedstock; and include excess carbon, sulfur, ash, soot, metal oxides, tars and low levels of impurity gases (CO_2, H_2S, CH_4, NH_3, HCN, N_2, and Ar). The formation of tars is a serious limitation to the use of biomass as a carbon feedstock. Tars, defined as a complex mixture of condensable hydrocarbons that includes single ring to 5-ring aromatic compounds [4-6], are viewed as an environmental hazard, and can adversely impact processing equipment, including the fouling of heat exchanger tubes. Depending on the application for the syngas, impurities can be removed at the gasification facility using a variety of chemical processing techniques that are located downstream from the gasifier vessel.

Types of Commercial Gasifiers

A number of different gasifier designs are used commercially, with the residence time for carbon feedstock in the gasifier varying from seconds to about 45 minutes, depending on the gasifier type. Three of the most commonly used types are shown in figure 2. All gasifiers thermally break down organic matter in the carbon feedstock according to equation 1; while inorganic materials (impurities) remain as a solid. Some gasifiers operate at temperatures low enough to maintain the solid waste as a “dry” ash (below the fusion temperature), while others operate at elevated temperatures that cause it to become molten and flow down the sidewalls of the gasification chamber as slag. For gasifiers that must operate at elevated temperatures because of high melting point, high viscosity ash; a flux can be added to lower the slag fluidity temperature.

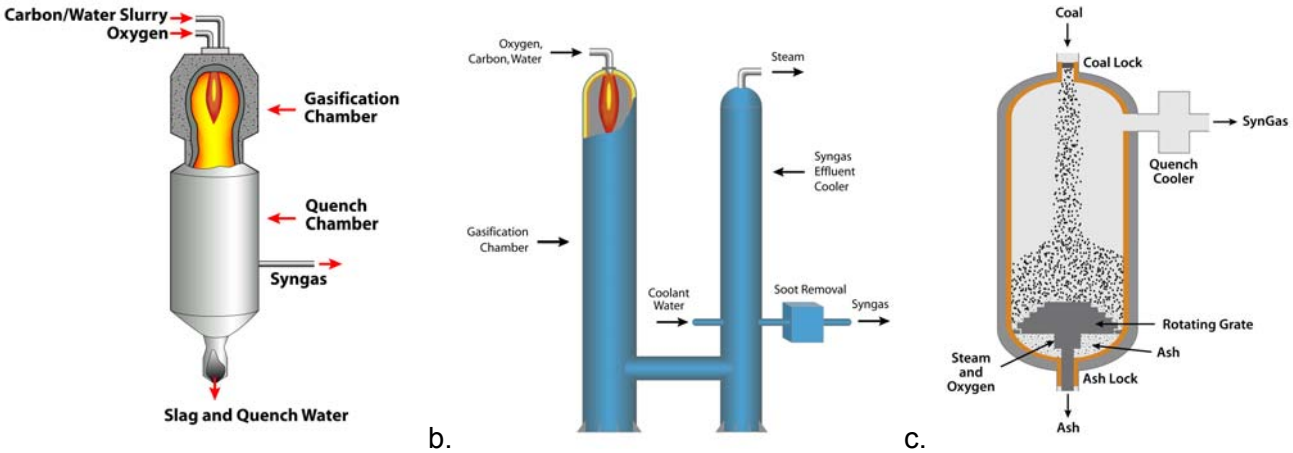

Figure 2 – Several designs of commercially used gasifiers: a) Entrained bed, b) Entrained bed, and c) Fixed bed dry-bottom gasifier.

Gasifier Feedstock

A variety of carbon feedstock have been used, or are being evaluated for use in gasification; including coal (all ranks - anthracite to lignite, and/or the liquidation residues), petroleum (including heavy oil, high sulfur fuel oil, and Orimulsion® [7]), petroleum by-products (oil distillates, residual oil, heavy oil, asphalt, visbreaker tar, refinery tar, heavy refinery feedstock, petroleum coke [delayed and fluid], refinery sludge, hydrocarbon fuels, refinery gas, bunker C-oil, vacuum residue, vacuum-flashed cracked residue, miscellaneous liquid waste, excess refinery products), natural gas, agricultural and municipal waste, liquor hazardous wastes (sewage sludge, biomass), and materials that are difficult to dispose of as waste (such as plastics and tires). A list of the gasifier types and/or manufacturer used at sites worldwide, and the carbon feedstock they utilize, is given in table 1 [8]. Petroleum, coal, gas, and petroleum coke currently fuel most of the gasification facilities (approximately 92 pct), with biomass and waste comprising the balance of carbon feedstock requirements. One design is used predominately for biomass gasification. Other gasifier designs exist or are being developed, however, some of which operate at temperatures high enough to liquefy ash impurities into slag. Regardless of the temperature of operation, biomass gasifiers require a refractory lining to protect the vessel shell.

Table 1 – Carbon feedstock in different types/manufacturers of gasifiers used or planned throughout the world [8].

Gasifier Type/Manufacturer	Carbon Feedstock Type (number of gasifiers utilizing)				
	Petroleum	Coal	Gas	Petcoke	Biomass/Waste
Entrained – manufacturer A	32	16	18	4	None
Entrained - manufacturer B	25	20	4	1	None
Entrained - manufacturer C	None	3	None	4	None
Fixed Bed - manufacturer D	None	6	None	None	None
Mixed – manufacturer E	None	None	None	None	6
Others*	2	6	1	None	7

* Other manufacturers of gasifiers with the number of them in use in parenthesis are as follows: manufacturer F (2), manufacturer G (2), manufacturer H (2), manufacturer I (2), manufacturer J (1), manufacturer K (1), manufacturer L (1), manufacturer M (1) manufacturer N (1), manufacturer O (1) manufacturer P (1), and manufacturer Q (1).

New gasification projects which target fuel flexibility (i.e., the ability to process variable feedstock) must take into consideration the anticipated ash fusion temperature, gasifier temperature, and the type of gas feed desired for the turbine or chemical feedstock when designing their facilities [9]. With any carbon feedstock, the gasifier should be strategically located to minimize transportation costs and maximize raw material availability. Other factors, such as those associated with carbon feedstock processing (grinding and beneficiation), must also be considered because of equipment costs and limitations. Interest has been gathering worldwide in the use of biomass, or other high carbon industrial wastes, as gasifier feedstock for a number of reasons, including: 1) it is considered a renewable energy source and helps meet Kyoto targets for reduced CO_2 emissions [10,11]; 2) many types of biomass are considered industrial wastes and have a disposal cost which helps offset the cost of gasification; and 3) biomass is available in most parts of the industrial world, including developing countries that have no coal or oil resources. Because significant issues remain with feedstock processing and ash chemistry/refractory liner interactions [12], the gasification of biomass is still considered a developing technology. The balance of this paper will focus on biomass and waste slag/refractory interactions.

BIOMASS AND WASTE GASIFICATION

Biomass is defined by Higman and van der Burgt [13] as any material that can be used as a fuel, or as a raw material for a fuel, that is derived from a recently living organism - a definition that excludes fossil fuels, but includes materials like agricultural and forestry wastes, black liquor, sewage sludge, and animal refuse. A partial listing of biomass and waste feedstock is given in table 2. Although not considered a major industrial fuel, biomass supplies 15-20 percent of the total fuel used in the world, primarily as a heating and cooking source in non-industrialized countries [13].

Table 2 – Biomass and waste feedstock used in gasification

Biomass	- Tree bark, timber block, sawdust, wood powder
	- Crop residue, husk, straw, corn stalks, soy straw, rice hulls
	- Coconut shell, ground nut shells, coffee husks, cocoa husks
	- Cotton residues
	- Palm oil shells, fibers, stems
	- Animal meat and bone, poultry litter
	- Black liquor
	- Marine crops
Waste	- Municipal solid landfill
	- Industrial solid and liquid by-product

The severe operating environment created by the gasification of biomass and other high-carbon waste materials creates a number of operational issues which limit the application of this technology. These issues are summarized in table 3. The source of biomass or waste feedstock must be consistently available in the quantity and consistency needed for gasification, with the additional requirement that shipping distances for biomass should not be greater than 50 km from collection points [14]. Gasifiers, such as those shown in figure 2, require a carbon feedstock with a high energy density and with an appropriate particle size for feeding into the gasifier. A number of gasifier designs have been developed that are capable of processing biomass, and are similar to those shown in figure 3. They can accommodate a coarse feedstock and are generally designed to operate at temperatures below 900^{o}C. The low gasification temperature is preferred for biomass and waste because of the low melting point and highly aggressive nature of the residual ash, the reactivity of which increases with temperature. To keep the biomass ash from melting, some fluidized bed reactors operate at temperatures as low as 650^{o}C. Fluidized bed reactors are also used instead of entrained flow gasifiers because the short residence time (seconds) in entrained flow gasifiers can result in incomplete combustion of the biomass. Tar formation, as mentioned earlier, is an issue in the low operating temperature fluidized bed gasifiers, which results in clogged particle filters, impacts combustion

efficiency, and can pose an environmental hazard. Research is focused on a number of fluidized bed designs; including updraft, open core, downdraft, or circulating systems; to solve these issues [15, 16].

Table 3 – Issues associated with biomass and waste feedstock as a carbon feedstock in commercial gasifiers.

- Feedstock quantity, consistency, and availability
- Feedstock chemistry (pct carbon, ash, and moisture)
- Ash softening/fusion temperature
- Hazardous material nature of by-products, including ash and tars
- Ability to process biomass as a gasifier feed
- Shipping distances (feedstock to gasifier)
- Compatibility with existing gasification process
- Feedstock energy density
- Ease of gasification

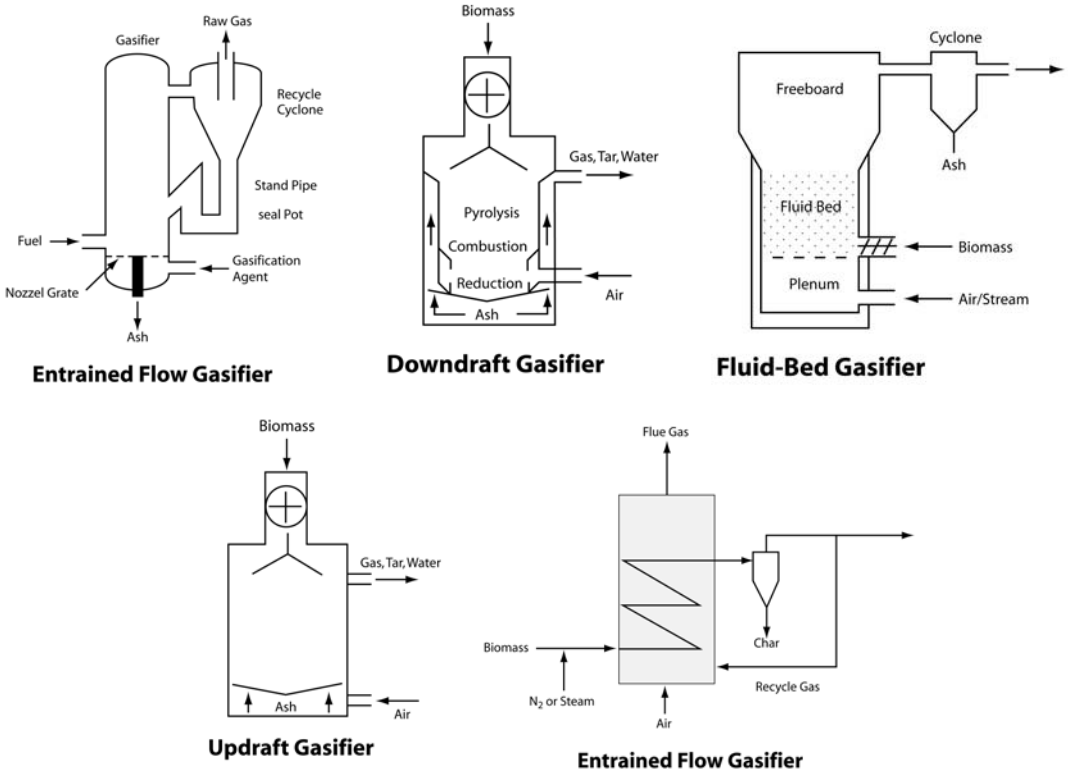

Figure 3 – Gasifier designs used in biomass gasification.

Ash chemistries for several biomass and waste gasifier feedstock are shown in table 4 [17]. The composition of the ash determines its melting point, and is also dependent upon the relative oxidizing or reducing conditions in the gasifier. The ash softening and melting points have a direct influence on the gasifier type, its operational temperature, and the materials used to construct it. In addition, some ash components, such as the alkalis, have a tendency to volatize under some gasification conditions, and can deposit deep within a refractory lining. Limited research has been conducted on refractory liner materials to identify acceptable materials for application in biomass gasifiers, but the variable nature of each biomass slag makes this a daunting task, since each slag must be considered for its possible interactions with the gasifier lining. Research has also been done to explore the use of mixed feedstock (coal or petcoke with low percentages of biomass) in commercial entrained flow gasifiers. In general, biomass feedstock such as those listed in table 4, are gasified in

fluidized bed gasifiers operating between 650- 1000°C. Limited trials converting biomass to carbon through pyrolysis, than using it as a gasifier feedstock, have also been conducted.

Table 4 – Ash chemistry of some select biomass feedstock [17]

Property (Wt %)	Material					
	Rice Straw	Wheat Straw	Switch Grass	Sugar Cane Trash	Sugar Cane Bagasse	Douglas Fir Wood
% Cl (dry wt biomass)	0.7	2.0	0.1	0.2	0.03	0.01
% Ash (dry wt biomass)	19.5	13.0	9.0	5.0	2.4	0.5
Oxides (in Ash) - Al_2O_3	1.4	2.5	4.5	NL	17.7	2.8
CaO	1.6	4.7	5.6	13.1	4.5	37.1
Fe_2O_3	0.7	1.0	2.0	1.7	14.1	4.2
K_2O	11.3	18.3	11.6	13.4	4.2	17.0
MgO	1.9	2.5	3.0	4.3	33	5.9
Na_2O	1.9	10.5	0.6	0.3	0.8	3.2
P_2O_5	2.7	1.5	4.5	2.3	2.7	1.9
SiO_2	74.3	35.8	65.2	57.4	46.6	12.3
TiO_2	0.02	0.2	0.2	NL	2.6	0.1
SO_3	0.8	5.5	0.4	7.3	2.1	11.2
Unknown	3.4	17.6	2.3	0.3	1.4	4.4

NL = Not Listed

REFRACTORY ISSUES IN BIOMASS AND BLACK LIQUOR GASIFICATION

The most challenging operating environment for a refractory lining is possibly that created by the gasification of black liquor. Black liquor is a byproduct of the kraft process used to separate wood fibers in papermaking. Recovery of the chemicals used in the process (sodium sulfide and sodium hydroxide) is currently performed in Thompson recovery boilers [18]. However, gasifiers offer a potential replacement for these boilers because they provide the added capability of producing electrical energy from the residual carbon in the black liquor, while recycling the raw materials for reuse. Two principal gasification processes have been utilized to gasify black liquor; 1) a low temperature process that takes place at about 600°C at atmospheric pressure; and 2) a high temperature process that occurs between 900◦ and 1000°C and higher pressures. In the low temperature process, solid salts form from the black liquor which do not directly corrode the refractory liner, but subject it to thermal, chemical, and mechanical effects [19]. In the higher temperature process, the inorganic salts impinge and liquefy on the gasifier refractory wall, flowing down it. Both liquid and gases are removed by a periodic quench.

Refractories used in the high temperature (1000°C) black liquor gasifier must act as both a chemical and thermal barrier to protect the metal cooling tubes and/or the gasifier sidewall. Sintered alumina-silica brick and fusion cast α/β alumina refractories have been evaluated as refractory liners for one type of air-cooled high temperature gasification process (1000°C), but were limited to a service life of 12 months or less [19]. Attempts to use water-cooled refractory linings in the high temperature gasifiers (similar to that used by Shell in figure 2-b) did not perform any longer. Hemrick et al [19] calculated that the black liquor smelt was 60-75 % Na_2CO_3, 20-38 % Na_2SO_4, 1-4 % Na_2S, and 1-4 % $Na_2S_2O_3$ during gasification, and used this composition range as an exposure media for evaluating refractory test samples at temperatures from 900-1000°C. A summary of these results is given in table 5, and indicates that in lab tests, fused cast α/β Al_2O_3, fused cast MgO/Al_2O_3 spinel, and MgO or Al_2O_3 ram mixes all show promise for black liquor applications.

Table 5 – Test results from exposing refractory materials to molten salts (60-75 % Na_2CO_3, 20-38 % Na_2SO_4, 1-4 % Na_2S, and 1-4 % $Na_2S_2O_3$) simulating black liquor gasification at 900-1000°C for times up to 50 hrs [19].

Type Gasifier	Refractory	Exposure Results
High temp., atm pressure	Fused cast α/β Al_2O_3	Good
	Fused cast MgO/Al_2O_3 spinel	Good
	Sintered MgO/Al_2O_3 spinel	Not as good as fused spinel
	Porous surface sealed – Li_2CO_3	Mixed results, inconclusive
High temp, above atm. pressure	Al_2O_3 coatings on metal coil	Poor, cracking
	MgO coatings on metal coil	Good
	Al_2O_3 ram mix	Good adhesion, good vapor resistance
	MgO castable	Good adhesion, good vapor resistance

Modeling of the black liquor gasification process by Rezaie et al [20] indicated that it will combust, leaving a smelt composed of 70-75 % Na_2CO_3, 20-25 % Na_2SO_4, and 2-5 % K_2CO_3. This smelt will be in direct contact with the gasifier sidewalls, requiring a liner material that is chemically resistant to it. Thermodynamic modeling of smelt in contact with refractory linings predicts that aluminosilicate refractories will react to form expansive phases (volume expansion up to 30 pct), followed by cracking and spalling, and resulting in significant material loss. The high volume expansion caused not only cracking and spalling, but also exposes sub-surface material to attack, hastening material degradation. The porous microstructure of the aluminosilicate refractories will further promote liquid alkali penetration that leads to the formation of low melting phases from refractory/slag interactions. Attack by the smelt is not limited to aluminosilicate refractories, alkalis will also interact with α-Al_2O_3, causing it to recrystallize into β-Al_2O_3, with an accompanying high volume expansion and material loss. The extent of interaction between fireclay or high alumina refractories and $NaCO_3$ depends on the temperature, and typically results in the formation of a complex series of phases.

Rezaie et al [20] also found that refractories composed of silicate, zircon, AZS (alumina-zirconia-silicate), and silicon nitride were vigorously attacked by the black liquor smelt, whereas fused spinel (MgO-Al_2O_3) refractories were found to interact with $NaCO_3$ only at the surface (due to the lack of porosity in the refractory material). Zircon refractory materials ($ZrSiO_4$) were found to react with Na_2CO_3 to form ZrO_2 and a sodium silicate glass. Interactions were noted to start at 1100°C, with continued exposure to Na_2CO_3 forming Na_2O-ZrO_2-$2SiO_2$, or other phases of increasing Na_2O content that occurred in layers within the brick surface microstructure. Zircon refractory exposed to Na_2SO_4 resulted in the formation of two phases, ZrO_2 and Na_2O-ZrO_2-$2SiO_2$. Interactions between AZS and Na_2CO_3 vapor led to the formation of new, low melting glasses with large volume expansions, followed by material failure. Nepheline (Na_2O-Al_2O_3-$2SiO_2$), canegieite (Na_2O-Al_2O_3-$2SiO_2$), and Na_2O-ZrO_2 were formed; causing extensive surface spalling. The presence of water vapor with Na_2CO_3 vapor allowed the formation of NaOH, leading to chemical dissolution of the AZS brick.

Thermodynamic calculations indicate magnesia refractories could be stable in the black liquor smelt [20]; however, concerns exist about the stability of the silica bond ($2MgO$-SiO_2) joining magnesia grain. This bond could be destroyed by interactions with Na_2CO_3, forming Na_2O-MgO-SiO_2.

Laboratory research using sessile drop testing to supplement thermodynamic data for Na_2CO_3 and K_2CO_3 interactions with refractory oxide materials at 1000°C in Ar (simulating slagging black liquor gasifier conditions) are summarized in table 6 [21]. Based on these observations, all materials chosen for evaluation had contact wetting angles (less than 90°); indicating potential for use as a non-wetting material, but many materials reacted with the molten salts during the tests and were therefore ruled out. Good contact angles with no interactions were found with CeO_2 (testing discontinued because of high

material cost) and MgO; stable contact angles, but with unstable phase formation (large expansive phases) were observed at the surface of ZrO_2, Y_2O_3, $3Al_2O_3$-$2SiO_2$, $LiAlO_2$, and $BaAl_2O_4$; and good contact angles with stable second phase formation were observed between the molten salts and $MgAl_2O_4$. Refractory materials containing $3Al_2O_3$-$2SiO_2$ were found to interact with Na_2CO_3 to form $Na_2Al_2SiO_6$, with a calculated volume expansion of 12 pct; while α-Al_2O_3 formed $NaAlO_2$, with a calculated volume expansion of 46 pct. Even though the refractory phase of $MgAl_2O_4$ interacted with the alkali carbonate salts, it was thought to offer better potential for service over MgO because of its hydration resistance.

Table 6 – Sessile drop contact angle and surface interaction between molten salt and select refractory materials at 1000°C in Ar [21].

Material	Salt	
	Na_2CO_3	K_2CO_3
	Contact angle/Surface interaction	Contact angle/Surface interaction
$MgAl_2O_4$	13°/Reacted	3°/Reacted
CeO_2	8°/No reaction	7°/No reaction
α-Al_2O_3	7°/Reacted, expansive phase	NA
MgO	4°/No reaction	10°/No reaction
ZrO_2	4°/Reacted, expansive phase	NA
Y_2O_3	2°/Reacted, expansive phase	NA
$3Al_2O_3$-$2SiO_2$	1°/Reacted, expansive phase	NA
$LiAlO_2$	NA	6°/Reacted, expansive phase
$BaAl_2O_4$	0°/Reacted, expansive phase	0°/Reacted, expansive phase

NA = Not analyzed

High chromia/alumina refractories (70 wt pct or higher Cr_2O_3) are widely accepted as the best available liner material for air-cooled slagging gasifiers using coal or petcoke as a carbon feedstock [21-23]. Use of these materials in gasifiers of the type shown in figure 2-a has become the industry standard, with gasification temperatures between 1250-1575°C, a temperature determined to a large extent by the fluidity temperature of the slag. Refractory failure is typically by two means: slag infiltration into the porous surface of the refractory, followed by spalling; or by chemical dissolution of the refractory into the slag [12]. The high chrome oxide materials also have potential for use in biomass gasifiers; however, the potential for alkali vapor attack of the refractory must be considered. Research conducted on alkali vapor attack (vapor originating from coal slag) of high chromia/alumina refractories between 927 and 1327°C indicated severe vapor attack of the refractory microstructure could occur [24, 25]. Evaluation of the performance of 90 wt pct Cr_2O_3/10 wt pct Al_2O_3 refractories subjected to vapor attack from Na_2CO_3 or K_2CO_3 at 900-1000°C showed that the chromia/alumina refractories are subject to disruptive volume expansion, or the formation of low melting liquids phases, leading to material failure under these conditions. It was noted that thermodynamic calculations indicated that Na_2O-Al_2O_3/Na_2O-11 Al_2O_3 or K_2O-Al_2O_3/K_2O-$11Al_2O_3$ would form in the high chromia/alumina brick at 927°C, these phases were not observed in laboratory tests. Similar exposure tests at higher temperatures (1022-1327°C), however, resulted in the formation of Na_2O-Al_2O_3/Na_2O-$11Al_2O_3$ or K_2O-Al_2O_3/K_2O-$11Al_2O_3$, confirming thermodynamic calculations. It was noted that after reacting with the alkali and chemical spalling occurred in the samples due to differences in thermal expansion. Spalling occurred most at the surface of the material, where alkali concentrations were the highest and the most Na_2O-Al_2O_3 was formed. It was also noted that exposure to low concentrations of Na_2O resulted in the formation of β-Al_2O_3, which does not have as disruptive a volume change as the sodium aluminate phases discussed earlier. The penetration depth of the vapor into the refractory increased with time and temperature, with sodium found to penetrate more than potassium. Although susceptible to alkali vapor attack, it was noted that chromia/alumina refractories were resistant to corrosion by sulfur in the temperature range evaluated.

Based on experience with coal, some refractory/slag/vapor interactions that were summarized as concerns in early research [26] should be considered when selecting refractories for biomass or waste gasification. These concerns include H_2/SiO_2 interactions (equation 2) and CO breakdown catalyzed by Fe_2O_3 (equation 3). The formation of SiO in equation 2 was noted to actively occur at temperatures of 980°C, resulting in SiO_2 deposition downstream where reoxidation of SiO occurred. The reaction of CO to form C (in the presence of Fe_2O_3 which is a known catalyst) causes carbon buildup in refractories below 730°C, and can result in the destructive breakup of the microstructure in the material. Testing procedures for evaluating the ability of a refractory to withstand a CO atmosphere have been developed [27] but are not commonly utilized. Because of syngas interactions with silica and iron, refractories low in these materials should be considered for use in biomass gasification.

$$SiO_2 + H_2 \rightarrow H_2O + SiO \quad \text{[equation 2]}$$

$$2CO \rightarrow CO_2 + C \quad \text{(reaction in the presence of } Fe_2O_3\text{)} \quad \text{[equation 3]}$$

SUMMARY AND CONCLUSION

A number of gasification technologies are commercially used to gasify coal and petcoke feedstock. Biomass constitutes a potential carbon feedstock for gasification, but the technology has not yet been fully developed; and as a result, only a small number of gasifiers have been commercialized for it or other waste materials. Limiting factors for biomass and waste gasification include techniques to process biomass to a usable particle size range for application as gasifier feedstock; the potential formation of tars in the syngas because of the gasification process, and the severe interactions of the biomass ash with the gasifier liner materials. High temperature gasification of biomass is an ideal way to eliminate tar formation in the biomass syngas, but the molten slag formed from biomass ash can have severe interactions with the gasifier liner, limiting gasifier lining life to one year or less. In applications such as black liquor gasification, experience shows that the on-line availability of the gasifier can suffer significantly because of the downtime brought about by poor performance of the refractory materials. Alkali in the slag can interact with the refractory to form disruptive expansive phases, or can interact with the refractory to form low melting phases. Either mechanism leads to material failure and unscheduled downtime of the gasifier for refractory replacement. As a result, the need exists for the development of improved performance refractory liners for biomass or waste gasification. Improved materials will have controlled porosity, an engineered coarse and fine grain microstructure, the ability to operate at temperatures as high as 1575°C, and the ability to resist interactions with the slag. Several refractory compositions have been identified with potential for use in slagging systems; however more work is needed to confirm their performance.

REFERENCES

1. N. Richter; Introduction to Gasification (ChevronTexaco); internet website: www.gasification.org/Docs/02Richter.pdf; August 2, 2005.
2. Information available from UHDE website: www.uhde.biz; The Shell Gasification Process; August 10, 2005.
3. General information from the website for Shell Gas and Power; internet website: www.shell.com; August 1, 2005.
4. Y. Cao, Y. Wang, J.T. Riley, and W. Pan; A Novel Biomass Air Gasification Process for Producing Tar-Free Higher Heating Value Fuel Gas; Fuel Processing Technology, vol. 87 (2006), pp 243-253.
5. M. Asadullah et al; Gasification of Different Biomasses in a Dual-Bed Gasifier System Combined with Novel Catalysts with High Energy Efficiency; Applied Catalysis A: General; vol. 267 (2004), pp 95-102.
6. T. Nordgreen, T. Liliedahl, and K. Sjostrom; Metallic Iron as a Tar Breakdown Catalyst Related to Atmospheric, Fluidized Bed Gasification of Biomass; Fuel; vol. 85 (2006), pp 689-694.

7. F. Marruffo, M.L. Chirinos, W Sarmiento, S.A. Bitumenes; Orinoco, and E. Hernandez-Carstens; Orimulsion® A Clean and Abundant Energy Source; presented at the 17th Congress of the World Energy Council; Houston Texas; September 14, 1998; information available from the website for the World Energy Council internet website: www.worldenergy.org.
8. Information from the Gasification Technology Council; internet website: www.gasification.org; August 10, 2005.
9. H. Jaeger; 630 MW IGCC Targets Cost Parity at $1600/kw and 38.5 % Efficiency; Gas Turbine World; Vol. 35, No. 2 (September-October 2005); p. 18-24.
10. E. Andersson and S. Harvey; Comparison of Pulp-Mill-Integrated Hydrogen Production from Gasifier Black Liquor with Stand-Alone Production from Gasifier Biomass; Energy (2006), doi:1016.06.021/j.energy.2006.06.021.
11. J. Lin; Development of a High Yield and Low Cycle Time Biomass Char Production System; Fuel Processing Technology, vol. 87 (2006) pp. 487-495.
12. K.S. Kwong, J.P. Bennett, C. Powell, and R. Krabbe; The Improvement of Slagging Gasifier Refractories; Proceedings of UNITECR 2005; Orlando, FL, USA; Nov., 2005, proceeding published by the American Ceramic Society.
13. C. Higman and M. van der Burgt; Gasification; Elsevier, Burlington, MA; 2003; 391 pp.
14. C. Franco, F. Pinto, I. Gulyutlu, and I. Cabrita; The Study of Reactions Influencing the Biomass Steam Gasification Process; Fuel, vol. 82 (2003), pp 835-842.
15. D. Leung, X. Yin, and C. Wu; A review on the Development and Commercialization of Biomass Gasification Technologies in China; Renewable and Sustainable Energy Reviews, vol 8 (2004), pp 565-580.
16. L. Rabou; Biomass Tar Recycling and Destruction in a CFB Gasifier; Fuel; vol 84 (2005), pp 577-581.
17. B. Jenkins, R. Bakker, and J. Wei; On the Properties of Washed Straw; Biomass and Bioenergy; vol. 10 (1996), no. 4, pp 177-200.
18. W. Headrick and A. Rezaie; Refractory for Black Liquor Gasifirs; USDOE Award no. DE-FC26-02NT41491 quarterly report issued Dec. 2003; 28 pp.
19. J. Hemrick et al; Refractory Testing and Evaluation at Oak Ridge National Laboratory for Black Liquor Gasifier Applications; Refractories Applications and News; vol. 9, no. 6 (Nov./Dec. 2004), pp 14- 20.
20. A. Rezaie et al; Interaction of Refractories and Alkaline Containing Corrodants; Refractories Applications and News; vol. 9, no 5 (Sept./Oct. 2004), pp 26-31.
21. A. Rezaie, W.L. Headrick, and W.G. Fahrenholtz; Identification of Refractories for High Temperature Black Liquor Gasifier; Proceedings of UNITECR 2005; Orlando, FL, USA; Nov., 2005, proceeding published by the American Ceramic Society.
22. Bakker, W.T., "Refractories for Present and Future Electric Power Plants," Key Eng. Mat, Vol. 88 (1993), pp 41-70.
23. Greenberg, S. and R.B. Poeppel, "The Corrosion of Ceramic Refractories Exposed to Synthetic Coal Slags by Means of the Rotation-Cylinder Technique: Final Report," research sponsored under USDOE/FE AA 15-10-10, April 1986, 66 pp.
24. K. Lee and J. Brown; Corrosion of Alumina-Chromia Refractory by Alkali Vapors: I. Thermodynamic Approach; Korean Journal of Ceramics, vol. 1 (1995), no. 1, pp 29-34.
25. K. Lee and J. Brown; Corrosion of Alumina-Chromia Refractories by Alkali Vapors: II. Experimental Approach; vol. 1 (1995), no. 2, pp 86-90.
26. N.S. Raymon and L.Y. Sadler; A Literature Review of Reactions Involving High-Temperature Gas and Alkali Metal Vapors; US Bureau of Mines IC 8721; 22 pp.
27. Standard Test Method for Disintegration of Refractories in an Atmosphere of Carbon Monoxide; ASTM test C-288-87; Annual book of ASTM Standards, 2002; Section 15, General Products, Chemical Specialties, and End Use Products; Volume 15.01; Refractories, Activated Carbon, Advanced Ceramics; ASTM International, West Conshohocken, PA, USA.